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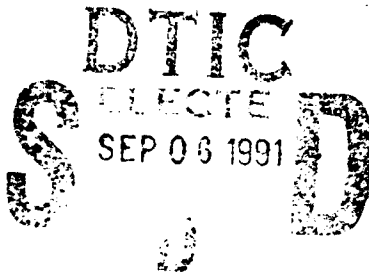
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Heat Generating Compositions for Thermal Batteries

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HEAT GENERATING COMPOSITIONS FOR THERMAL BATTERIES

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V. N. Sheptunov

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EDITOR'S SUMMARY

The requirements for heat sources in thermal batteries are described and different heat generating compositions are reviewed.

LIST OF CONTENTS

	Page
Text	3
References	10

Thermal batteries are widely used as independent current sources with long storage life and the ability to operate over a wide ambient temperature range of -54 to $+71^{\circ}\text{C}$ ¹. A number of pyrotechnic materials may as a rule be used as sources of thermal energy to provide ionic conduction in a molten electrolyte and to maintain the working temperature of the battery during the discharge of the electrochemical elements (EKhE).

The reliability of ignition of the heat generating elements (NE) is a fundamental problem which requires a solution before they may be considered for use in thermal batteries. In this connection it is reckoned that a fundamental item in the technical specification of a thermal battery is the activation time, ie the time from the moment of application of the electrical impulse to ignite the NE to the moment of achieving maximum power from the EKhE². The activation time of thermal batteries is substantially influenced by such factors as the choice of pyrotechnic material, the ratio of combustible and oxidant, the quantity of heat given out by the combustion of the NE, the thermal conductivity of the pyrotechnic material, and the melting temperature of the electrolyte of the EKhE. Also, the rate of burning of the NE depends upon the particle size distribution of the combustible, the temperature of decomposition of the oxidant, the quality of mixing and the mass diffusion rate of the components of the NE^{3,4}. The pyrotechnic material must meet the following requirements: the components of the NE must be stable, non-hygroscopic and compatible with each other; it must readily ignite and give negligible emission of gases while burning; its rate of burning must be relatively insensitive to changes in pressure and initial temperatures; over long-term storage there must be no changes in its working properties. The NE must withstand vibration, impact and other loads⁵⁻⁷. Introduction of various binding materials into the NE improves its performance. However among the products of combustion there are gaseous components (H_2 , CO , CO_2 , N_2 , H_2O , O_2), which are formed at high temperature, and also exist in traces in the original combustible materials^{1,5,6,8}. Thus H_2 , which possesses the highest thermal conductivity, on penetrating the structure of the thermal insulating materials (TIM) of the thermal battery causes the rate of thermal loss to be doubled and as a consequence sharply reduces the operating time of the EKhE³. To prevent penetration into the TIM of the high-conductivity gases given out on activating the NE and during operation of the thermal battery, a filler gas is introduced under pressure into the porous TIM; its thermal conductivity (λ) is less than that of air. The filler gas must be inert with respect to the EKhE and not be converted into other solid substances in the temperature range -55 to $+600^{\circ}\text{C}$ and at pressures of between 0.1 to 2 MPa. This requirement is met by the inert gases (Ar, Kr, Xe) and certain halogen-substituted hydrocarbons

(CF_4 , C_2F_6 , etc). To achieve this the TIM is subjected either to vacuum or filling with gases of low λ . Thus by having the TIM in a sealed layer¹ it is isolated from gases given off during the combustion of the NE, and from those formed during the functioning of the EKHE block. Water vapour formed on activation of the NE may be absorbed by $\text{Mg}(\text{ClO}_4)_2$, P_2O_5 , zeolite and other absorbents introduced into the TIM⁸. As an example, on burning a heat generating mixture made up of 62.9% by weight Zr, 11.1% BaCrO_4 and 26% FeCrO_4 , the proportion of gas given off amounts to $7.5 \cdot 10^{-3} \text{ m}^3/\text{kg}$. The rate of burning of the heat generating mixture does not exceed 0.71 m/s ¹⁰. From the combustion of an NE made up of 88% by weight Fe and 12% KClO_4 , $5 \cdot 10^{-6} \text{ m}^3$ of H_2 per $1 \cdot 10^{-3} \text{ kg}$ of pyrotechnic mixture is given off. To combine with the H_2 given off by an NE of mass $3.8 \cdot 10^{-3} \text{ kg}$ requires $1.8 \cdot 10^{-5} \text{ kg}$ of powdered CuO , which may be situated in the thermal battery between the NE and the EKHE. After the chemical combination of the H_2 by means of an oxidant the operating time of the thermal battery is increased by more than a factor of two⁸⁻¹¹. An oxide or an oxygen-containing salt may generally be employed as an oxidant for NE; however instead of oxygen, fluorine^{5,6} may be used. The latter, on combination with Mg or Al for example, gives out more heat than on combination with O_2 . At Ref 12 an NE composed of a powdered mixture of Mg and polytetrafluoroethylene (Teflon) is employed. On activation an exothermic oxidation-reduction reaction occurs in the NE: $(\text{C}_2\text{F}_4)_n + 2n\text{Mg} \rightarrow 2n\text{C} + 2n\text{MgF}_2$. By calculation, the heat derived from the combustion of the NE amounts to 9.6 kJ per $1 \cdot 10^{-3} \text{ kg}$ of the mixture¹³. However, as a combustible, Mg must be used with care as it is susceptible to moisture which causes the working properties of the NE to be degraded, as well as making difficult its ignition and the spreading of the flame front. Following long storage, the effect of moisture in the NE becomes more pronounced. Instead of Mg, therefore, it is advisable to employ zirconium, alloys of zirconium and nickel, titanium, molybdenum and other metals and alloys. However these metals undergo oxidation in the presence of moisture; consequently following storage the burning time of samples is increased. Treatment of these combustibles with chromates, and the use of other coatings did not lead to the desired results. In Ref 5 the conclusion was reached that the only means of obtaining uniformity and stability in the properties of NE materials was to store them in a dry atmosphere.

Depending upon the particular constructional features of thermal batteries the solid products of combustion of the NE in the heat generating composition may be either electrically conducting or not. For example, to prepare a non-conducting NE employing Zr and BaCrO_4 , a two-layered structure is employed with

both a thermally insulating and a pyrotechnic layer. Material for the thermally insulating layer may be asbestos or glass fibre, ceramic, Al_2O_3 , or other materials in powder form.

To prepare a two-layered NE the following technique¹⁴ is employed. Asbestos fibre or other powdered material amounting to $2 \cdot 10^{-2}$ kg is mixed with $1.5 \cdot 10^{-4}$ m³ of water. The suspension obtained is deposited on paper, fabric or a metal mesh. The thickness of the thermal insulating layer of the NE on its paper base comprises $2 \cdot 10^{-4}$ m. A layer of heat generating mixture made from $2.6 \cdot 10^{-2}$ kg Zr, $7.4 \cdot 10^{-2}$ kg BaCrO_4 , $1 \cdot 10^{-2}$ kg asbestos fibre and $0.5 \cdot 10^{-4}$ m³ H_2O , prepared by a method in which the solids are precipitated on to the thermal insulating layer, has a thickness of $1 \cdot 10^{-3}$ m. The two-layer NE is dried under vacuum at 70°C to remove moisture.

A single-layer non-conducting NE may be obtained in the following manner: 30% by weight Zr, 70% BaCrO_4 and a small quantity of asbestos fibre are mixed in water¹⁵, then the solids are separated by vacuum filtration and dried. The NE is placed in metallic dumb-bells made of nickel, to act as current collectors for the Mg anode. The catholyte of the EKHE consists of 65% by weight V_2O_5 and 35% of a eutectic of LiCl-KCl ; the electrolyte consists of 65% by weight of a eutectic mixture of LiCl-KCl and 35% kaolin acting as a binder. The activation time of a thermal battery containing this NE is 0.4 s.

Glass fibre forms a basis for the manufacture of non-conducting NE; a layer of suspension is placed on it, the latter consisting of an aqueous mix of inorganic silicate and powdered heat generating mixture¹⁶. The NE obtained is passed through a drying oven. The silicate assists in the adhesion of the heat generating powder to the glass fibre. For operation in thermal batteries a non-conducting NE is used which consists of a mixture of Zr as reducing agent and SiFe , together with an oxidant, either a metal chromate or a mixture of one with KMnO_4 ¹⁷. In preparing NE of this composition carboxymethylcellulose and water are added as a binder. After mixing together, the material obtained is shaped and dried. A dry method may be employed as an alternative to the wet mixing^{13-15,18,19} of the constituents of a non-conducting NE based on Zr and BaCrO_4 . For example, glass may be added in the form of powder, fibre or fabric²⁰ to the above NE. On heating, the glassy part of the NE melts, and at the completion of burning, it hardens. A glass made up of Na_2O and K_2O , and amounting to 0.5% by weight, is added to a mixture of 54.4% SiO_2 , 14.4% Al_2O_3 , 7.8% B_2O_3 and 21.9% CaO . The melting temperature of the glass does not exceed 700°C. On activation such a mixture rapidly heats up to 1000°C, the glass melts, and when the temperature of the NE falls to 400 to 600°C the mass hardens. The presence

in the NE of the oxides of calcium, sodium and potassium protects the combustible material from the influence of moisture.

There are a number of methods of preparing an NE which is conducting only during the activation of the EKhe. For example, non-conducting NE made from zirconium, barium chromate and an inorganic binder, after the introduction of a eutectic mixture of LiCl-KCl, becomes conducting when the latter melts; this also fulfils the function of a thermal accumulator as well as reducing overheating of the EKhe and increasing the operating time of the thermal battery^{2,21,22}. The cathode of the EKhe may be made of nickel or have an electrodeposited layer of gold; the depolariser, iron sulphate, and the anode, calcium². An NE based on nickel and sulphur, non-conducting at room temperature, becomes conducting on ignition²³.

An NE based on metal/metal oxide which is non-conducting during storage, becomes conducting during combustion^{24,25}. As a combustible in the NE one may use finely-divided powdered metals possessing low formation energy of the oxide, such as Fe, Co, Ni, Cr, Mo, Al, B, Mg, Ti, Zr and Ta. The oxidant may be a higher oxide of a metal of variable valency, for example WO_3 or MoO_3 , while a lower metal oxide must possess high conductivity. The inclusion of a metal in the NE must enable the reduction of a higher oxide to one of the lowest, for example $\text{WO}_3 \rightarrow \text{W}_2\text{O}_5 \rightarrow \text{W}_4\text{O}_{11} \rightarrow \text{W}_2\text{O}_3 \rightarrow \text{WO}$. The calorific value and the rate of burning of the NE is determined by the extent of the reduction reaction on the metal oxide. Inert fibrous material such as asbestos, and a diluent such as sand, is also introduced into the composition of the NE. The amount of such additives must not exceed 40%. The specific resistance of NE pellets made up of 25% by weight Zr, 57% WO_3 and 18% glass and ceramic fibre, is $1.6 \cdot 10^8 \text{ ohm/m}^2$, while the specific resistance of the fused material does not exceed $1.6 \cdot 10^2 \text{ ohm/m}^2$ (Ref 24).

Consideration is given²⁵ to NE consisting of powdered metal, an oxidant such as the chlorate or nitrate of an alkali metal, and a diluent, while to achieve conductivity of the products of combustion of the NE the metal content is in excess of the stoichiometric proportion. To initiate the NE an igniting composition containing 28% by weight Zr and 72% BaCrO_4 , which conserves its electrically insulating characteristics before and after burning is used. In certain instances an igniting composition is employed having a lower rate of burning, consisting of a mixture of Si, PbO_2 and CuO , in the ratios 4:3:3 respectively.

When using the above NE, the activation time of the EKhe does not exceed 1 second. This is determined by the fact that before the electrolyte of the EKhe

melts, the flow of heat on ignition of the NE must pass through the thermal barrier comprised of the metal current collector of the cathode and its mesh covered by the depolarising layer². Also, the activation time of the EKhe depends on the type of NE, the rate of its ignition and the quantity of thermal energy given out per unit time. It also depends upon the thermophysical characteristics of the EKhe, the NE, the metal current collectors and other elements of the thermal battery.

Table 1

Components of the mixture, %				Nominal mean burning time, s, under pressure, MPa				
Zr	Ni	BaCrO ₄	KClO ₄	140	210	280	350	420
5	20	64	11	11.0	11.2	11.8	12.1	12.2
12	13	64	11	-	-	2.0	2.0	1.9
4	21	64	11	13.0	13.5	14.0	14.3	14.0

It has been suggested that, in order to decrease the activation time of the EKhe, heat generating mixture should be introduced into the electrolyte^{2,26,27}. It was found that a pyro-electrolyte can give rise to an EMF in the EKhe within 0.2 to 0.3 second. However the time of operation of the EKhe with a pyro-electrolyte is of the order of 20 seconds².

Despite the generality of the technical solution proposed in Refs 2, 26 to 28, pyro-electrolytes excel in the composition of NE and electrolytes. In Ref 26 for example, a high-capacity EKhe intended for brief discharge modes contains in a solid eutectic LiCl-KCl electrolyte a heat generating mixture of Al and V₂O₅, which achieves uniform and rapid melting. The quantity of heat generating mixture is calculated for the thermal capacity of the whole EKhe, and on igniting it by a thermal cartridge the temperature of the element reaches 650 to 800°C. The electrolyte proposed in Ref 27 and 28 contains combustible components and has the following composition: 20 to 40% by weight KClO₄, 20 to 40% PbO₂, 10 to 30% Si, 10 to 20% LiCl and 2 to 8% PbCrO₄, with the PbO₂ and KClO₄ acting as oxidants for the combustible in the pyro-electrolyte. The KClO₄, on breaking down to KCl, fuses with the LiCl. The PbCrO₄ acts as depolariser for the EKhe. Either Ca or Mg may be used as an anode, and for a current collector, Ni.

many kinds of NE for thermal batteries are prepared by the compression method; they include NE based, for example of Ti-C , Zr-C , Zr-2B^4 , $\text{Ni-Zr-BaCrO}_4\text{-KClO}_4^{5,29}$, $\text{Fe-KClO}_4^{7,30,31}$, B-BaCrO_4^{12} , $\text{Zr-ScCrO}_4\text{-KMnO}_4^{32}$, $\text{Fe-Zr-KClO}_4\text{-BaCrO}_4^{33}$ and others. Before compression the components of the NE are uniformly mixed both dry and wet. NE made up of 15 to 35% by weight Zr, 30 to 70% PbCrO_4 and 5 to 40% KMnO_4 and prepared by the compression method gives off on burning an insignificant amount of gas, and there is no risk of destruction of the thermal battery³². An analogous three-component NE composition consisting of 15 to 45% by weight Zr, 30 to 65% SrCrO_4 and 5 to 40% KMnO_4 may be prepared by a method of compression within the range 0.3 to 1.25 MPa. Variation of the proportions of these components will change the burning time from 0.5 to 6.0 s/m³⁴. NE as prepared in Ref 32 and 34 is non-conducting both before and after activation.

A conducting NE, consisting of 90% by weight Fe and 10% KClO_4 , may also be prepared by the compression method. With these proportions the components of the NE were compressed at $P = 1.57 \cdot 10^5 \text{ N}^{31}$. On burning the NE, the calorific value was found to be 753.6 kJ/kg. In addition, the burning rate of the NE at room temperature was $29.46 \cdot 10^{-3} \text{ m/s}$, and at 53.3°C , $24.13 \cdot 10^{-3} \text{ m/s}$. The NE was ignited with fuse paper based on Zr and BaCrO_4 , having a calorific value of 1507.2 kJ/kg. On introducing 4% by weight Zr into the Fe-KClO_4 mixture, the sensitivity of the NE to ignition was increased. With the proportions 86% by weight Fe and 14% KClO_4 the calorific value amounted to 1067.6 kJ/kg, and here the rate of burning of the NE did not exceed 0.1 m/s^{30} . NE prepared from 88% by weight Fe and 12% KClO_4 by the compression method at $P = 5.89 \cdot 10^5 \text{ N}$ achieved a density of $3.6 \cdot 10^3 \text{ kg/cm}^3$, and the calorific value was 929.46 kJ/kg⁷. The conductivity of an NE based on Fe-KClO_4 and solid combustion products is due to a significant excess of combustible material relative to the stoichiometric proportions. As follows from Refs 7, 30 and 31, the calorific value and rate of burning of the NE rise with an increase in the quantity of oxidant. The degree of compression has an insignificant effect on the burning rate.

Table 1 demonstrates the negligible influence of the degree of compression on the burning rate of non-conducting NE made from a mixture of Zr, Ni, BaCrO_4 and KClO_4^5 .

A composition of finely divided powders made up of 5% by weight Zr, 22% Ni, 5.62% BaCrO_4 and 16.8% KClO_4 , following compression at $P = 5.89 \cdot 10^4 \text{ N}$ showed a rate of burning of 0.254 m/s and a calorific value of $2800.16 \text{ kJ/kg}^{26}$. Also, on igniting these NE, four exothermic reactions proceeded simultaneously (Table 2), each characterised by its own burning rate and calorific value⁵. By altering the

relative amounts of Zr and Ni, the burning time of the NE may be made to vary over a wide range (Table 1).

Table 2

Equation of chemical reaction	Stoichiometric proportions of components, %	Calorific value, kJ/kg
$\text{KClO}_4 + 2\text{Zr} \rightarrow \text{KCl} + 2\text{ZrO}_2$	43/57	6615.144
$\text{KClO}_4 + 4\text{Ni} \rightarrow \text{KCl} + 4\text{NiO}$	37/63	2512.080
$4\text{BaCrO}_4 + 3\text{Zr} \rightarrow 4\text{BaO} + 2\text{Cr}_2\text{O}_3 + 3\text{ZrO}_2$	79/21	1574.237
$2\text{BaCrO}_4 + 3\text{Ni} \rightarrow 2\text{BaO} + \text{Cr}_2\text{O}_3 + 3\text{NiO}$	74/26	184.218

The compression method may also be used for the preparation of four-component compositions of conducting NE, comprised of 66.35% by weight Fe, 4.07% Zr, 12% BaCrO_4 and 17.53% KClO_4 ³³. This is first mixed with alcohol in a ball mill. The addition of Zr increases the sensitivity of the NE to ignition. To ensure ignition of the compositions quoted at^{29,33} at sub-zero temperatures, it was necessary to introduce KClO_4 ⁵. The latter is employed not only in NE, but in ignition compositions such as those, for example, made up of 36% by weight Zr, 50% BaCrO_4 and 14% KClO_4 , which possess a speed of ignition of 0.1 second. On burning this pyro-mixture the quantity of gas given off does not exceed $1.10 \cdot 10^{-3} \text{ m}^3/\text{kg}$ ^{35,36}. An increase in the sensitivity of ignition and burning rate of this pyro-mixture is ensured not only by introducing KClO_4 into the composition, but by increasing the content of the combustible materials above the stoichiometric proportion (Table 2). In certain cases, however, with the object of reducing the sensitivity of finely divided combustible materials at ambient temperatures, they are subject to heat treatment at temperatures of between 148.9 and 426.7°C; during heating within this temperature range ignition of the composition must not occur. By this means heat treatment may be given to compositions containing red phosphorus or those metals whose oxides have a free energy of formation per gram-atom of oxygen which is more negative than 167.47 kJ, as well as inorganic oxidants having a free energy of formation per gram-atom of oxygen which is more positive than this value. Examples of such NE mixtures are Zr-BaCrO_4 , Mg-BaO_2 , $\text{P-KClO}_4\text{-Sb}_2\text{S}_3$ ³⁷. It is evident that significant attention requires to be paid to the means of preparation and the technical characteristics of types of NE of varying composition, as employed in thermal batteries.

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